Mechanism of pitch adsorption on carboxy methyl dextran surfaces

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SUMMARY

The direct adsorption of pitch particles onto pulp fibres was investigated as a pitch control strategy. The affinity of colloidal pitch for carboxyl methyl dextran (CMD) surfaces was studied by surface plasmon resonance (SPR) spectroscopy and optical microscopy. CMD was selected as model surface representing the cellulose and hemicellulose fractions of the pulp fibres. The dynamics of adsorption and desorption of concentration pulses of colloidal pitch on carboxy methyl dextran were followed at the solid-liquid interface in real time by SPR. The parameters investigated were temperature, pitch concentration and sequence of pitch build up. The direct adsorption of pure colloidal pitch onto pulp fibres is not an option for papermaking. This is because of the very low chemical affinity measured between pitch and the model CMD polysaccharide. Virtually no pitch remains adsorbed by chemical interaction on CMD surfaces submitted to low shear. In spite of its low affinity for polysaccharides, colloidal pitch can be carried by fibres as the low desorption rate might not allow full particle desorption during the time frame of the forming process, and some physical entrapment might also occur. Pitch has a stronger affinity for pitch covered surfaces than for polysaccharides.

KEYWORDS

Pitch adsorption, surface plasmon resonance (SPR), carboxy methyl dextran, liquid-solid interface, paper making.

INTRODUCTION

Pitch deposits has been a problem for the pulp and paper industry not only in Australia but worldwide, for many years. It is estimated that 1-2% of total annual sales, amounting to 3-5 billion US dollars, is lost due to pitch problems. Pitch deposits arise from the agglomeration of resinous material released from the wood in the pulping process. These deposits adversely affect paper machine efficiency and product quality. Furthermore, if large amounts of the resinous material are discharged into effluent, they pose an environmental problem because of their natural toxicity (*1-9*).

Norske Skog operates two mills in Australia, one at Albury in New South Wales and the other at Boyer in Tasmania. Both mills are on major rivers, the Murray River in New South Wales and the Derwent River in Tasmania. Both are in environmentally sensitive regions where water use and quality are of major concern. The need to reduce water consumption and increase process water recycling has exacerbated the pitch problem due to the build-up of organic and inorganic contaminants, in particular the wood resins that cause pitch problems. The degree of mill closure at the Norske Skog Albury Mill is limited due to the pitch concentration in the recycled process water.

The Albury mill has had ongoing pitch problems since it commenced operation in 1980. The wood extractives from *Pinus radiata*, in particular, result in colloidal aggregates that form pitch. The wood extractives are released from the wood during the TMP pulping process. The extractives, which mainly consist of resin acids, fatty acids, triglycerides and steryl esters, are lipophilic in nature and so tend to form colloidal aggregates that then deposit onto paper machine surfaces. A considerable amount of work has been undertaken to understand the causes (*1-8*) and find solutions to the problem of pitch deposition (*9-15*).

There are two extreme strategies for pitch control. The first consists of stabilising the colloidal pitch to keep it segregated into the process water (for later removal in the water treatment system); the second is to destabilise pitch for easier removal. Destabilisation can be engineered either by adsorption on a surface, or by coagulation followed by a separation unit, such as ultrafiltration or reverse-osmosis. An attractive pitch removal strategy is through direct adsorption onto the pulp fibres, wherein paper acts as a sink and pitch is sold as paper. The issues to optimise are fibre pick up in the press and calender sections, paper sizing and printability. This study investigates the feasibility of adsorbing colloidal pitch directly onto fibres, without polymeric aids. It is critical to measure the natural affinity that pitch has for cellulosic fibres. In this study, the adsorption dynamics of pitch particles at the solid-liquid interface is quantified in real time by Surface Plasmon Resonance Spectroscopy (SPR). Model systems and novel experimental techniques are used to gain a different perspective of the on-going pitch deposition problem. Carboxy methyl dextran (CMD) was selected as the model surface because it serves as a good representation for the micro-fibrils made of cellulose and hemicellulose; it allows the measurement of pitch retention by chemical interaction, without any contribution from physical entrapment. The effect of water temperature, pitch concentration, and sequential adsorption process on pitch adsorption is quantified by surface plasmon resonance using a BIAcore-X® instrument. The findings are then analysed in the context of papermaking and in terms of pitch control strategy.

BACKGROUND

A model of a pitch aggregate has been proposed in which the resin acid and fatty acids interact via hydrogen bonding to form an outer region around a core of the hydrophobic triglycerides and steryl esters (*6,8,16*) (Fig. 1). The carboxyl and hydroxyl groups of the resin and fatty acids extend into the water and stabilise the pitch aggregate. It is this outer region that is believed to control the chemical reactivity, charge, colloidal stability and deposition tendency of the pitch aggregate. The driving force for the deposition

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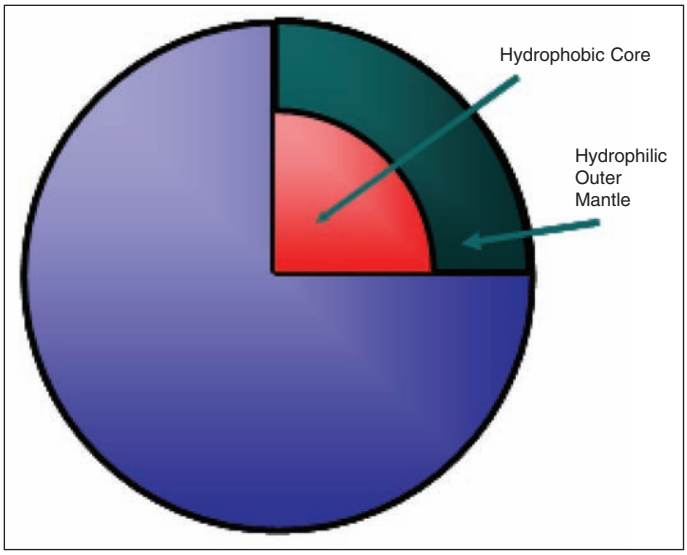

Fig. 1 Schematic representation of a pitch colloid [Vercoe (*6*) and Qin (*8*)].

of the aggregates is due to a combination of factors largely governed by process conditions. At low pH, when the pitch particles are uncharged, hydrophobic and hydrogen bonding type interactions control the interaction between the pitch aggregate and surfaces. At higher pH's, near pH 7, electrostatic interactions may play some role as the resin acids and fatty acids are partially ionised with the resin acids having pK_a above 6.5 and the fatty acids having colloidal pK_a above 7.0 (*17*). Surface energy measurements have shown that the resin acids and fatty acids have a higher acid-base component of the work of adhesion (*8*) and that the resin acids have a greater tendency to wet stainless steel and polyethylene surfaces.

The pitch particle size measured in a series of studies is presented in Table I; where five of the nine colloidal particle sizes are reported as a size range. The maximum reported particle size is 2 μm (*24*).

Table I
Particle size of softwood colloidal wood resins

Colloidal particle size (µm)	Literature Source
0.35	McLean et al (*18*)
0.8	Allen (*19*)
0.2	Wågberg and Ödberg (*12*)
0.54	Swerin et al (*20*)
<2	Shetty et al (*21*)
0.15-0.4 (mean 0.26)	Sundberg et al (*22*)
0.15-0.4	Nylund et al (*23*)
0.2-2	Allen (*24*)
0.1-1.5	Thornton (*25*)

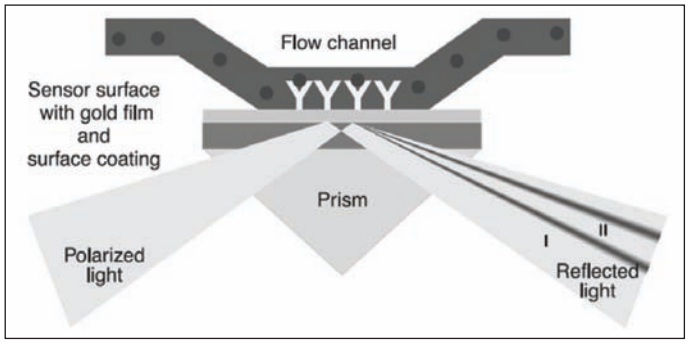

Fig. 2 Schematic representation of a Surface Plasmon Resonance Spectrophotomer (SPR) with the polarized light beam reflected under the carboxy methyl dextran coated gold film over which flows the eluent carrying pitch (*26*).

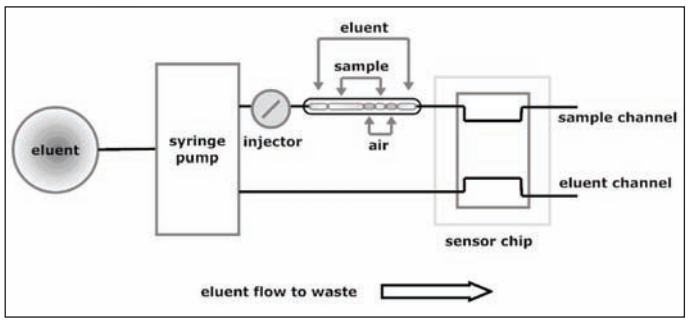

Fig. 3 Schematic of the flow path of the BIAcore-X® showing the two channel flow system.

EXPERIMENTAL

Methods

Surface plasmon resonance

Surface Plasmon Resonance Spectroscopy (SPR) allows real time measurement of material adsorption at the solid-liquid interface without labelling techniques. The SPR system typically consists of a flow system, a sensor surface, a light source and a SPR detector (Fig. 2). A polarised light is reflected on the gold coated sensor surface and detected by the diode array sensor (*27*). Light is reflected by a thin film of gold, stimulating the generation of resonance as the energy and momentum of the incident photons are converted to surface plasmons. Plasmons are electromagnetic waves resulting from the disturbance from equilibrium of large numbers of electrons in matter with a regular structure. For our experiments, carboxy methyl dextran chains are grafted on a gold film supported by a glass slide (sensor chip CM5). Changes in refractive index in the micro fluidic cell on the opposite side of the gold foil to the incident light, attenuates the surface plasmon resonance. SPR spectroscopy probes the change in refractive index caused by the adsorption of material in the cell. The resulting sensogram is a plot of the variation in SPR incidence angle as a function of time, which represents the evolution of mass adsorbed (pitch) at the solid-liquid interface.

The SPR used was a BIAcore-X®. The eluent is delivered via a controlled syringe pump to a micro-fluidic flow cell. The eluent is proportioned between two channels, one carrying the analyte sample and the other carrying only the eluent, serving as reference (Fig. 3). Both channels flow over the sensor chip surface where the change in refractive index of either or both (or the difference in refractive index between the two) can be determined as a function of time.

CM5 Sensor chips, having medium molecular chains carboxy methyl dextran chains (around 100nm) grafted on gold films over a glass slide, were purchased from BIAcore and used as is. 90μL aliquots of the pitch aqueous suspension were acquired using a 20-200μL

autopipette and injected directly into the inlet port of the BIAcore-X® (*26*). The eluent employed was Milli-Q® water filtered and degassed through a cellulose filter membrane under vacuum. This water also served as diluent for stock solutions. The eluent was kept at room temperature and delivered to the sensor chip surface by flow conduits and a syringe pump at a flow rate of 5 μL/min. Sensograms were obtained at 20°C and 30°C. The natural pH of the aqueous pitch suspensions was constant at around 5.5 and left unchanged; pH of the Milli-Q® water eluent was 6.5.

Sample preparation for optical microscopy

A conventional optical microscope equipped with a stage micrometer was used to estimate the size range of precipitated wood extractives particulates. A drop of aqueous suspension was delivered to a clean, dry microscope slide using a Pasteur pipette. A clean cover slip was placed over the drop. An Olympus BX-60 optical microscope was used to image particulates at different resolutions. Bright field lighting from above illuminated the samples. Images were captured with the SPOT Advanced software. Feature dimensions were added by calibrating the system with a stage micrometer and stamping the micrographs electronically.

Materials

Precipitation of wood extractives (large particles)

Pitch extracts in acetone were obtained using a modification of the method described by Sundberg (*14*). Wood resin from *Pinus radiata* TMP pulp was obtained by soxhlet extraction with hexane for a minimum of twenty cycles. The hexane was removed by rotary evaporation and the wood resins were then dispersed in acetone and stored at -4°C until needed. A 10.8 mg/mL solution of wood extractives from Pinus radiata TMP pulp in acetone resulted (*3-7*); this was used as is in the adsorption study. A colloidal dispersion of pitch was prepared by dispersing an aliquot of the wood resin in acetone solution in distilled water. For each SPR study, a colloidal dispersion of pitch particulates was obtained by mixing various 200 μL pitch/acetone aliquots (1, 2, 3 or 4) into 50 mL of Milli-Q® water under constant stirring for 10 minutes.

The composition of the wood resins was determined using a Varian 3800 Gas chromatogram using a 15m x 0.53mm ID x 0.15 µm film thickness ZB-1 GC column as previously described (*7*).

RESULTS

This study investigates the feasibility of directly adsorbing pitch particles onto pulp fibres prior to papermaking. Our aim is to quantify the chemical affinity of colloidal pitch for cellulosic surfaces, and to better understand the mechanisms by which pitch particles can directly interact with fibres. No retention aids or polymers were used. The association and dissociation dynamics of pitch suspensions onto carboxyl methyl dextran (CMD) surfaces was studied by surface plasmon resonance (SPR) spectroscopy. SPR was selected as it is not only a real time technique which does not require a labelling technique, but also because it is one of the most sensitive methods to probe the solid-liquid interface. SPR has the potential to measure the adsorption down to the individual molecule of fatty acid or resin acid forming pitch. Carboxy methyl dextran (CMD) was investigated as the surface, modelling the cellulose and hemicelluloses fractions of mechanical pulp fibres. Dextran has the same chemical composition as cellulose. However, the anhydroglucose units are linked by a combination of α- glycosidic bonds: α1-6 for the straight segments, α1-3 and α1-2 for the branches, instead of the unique β1-4 bond found for cellulose; resulting in a more soluble and a branched macromolecule. The carboxylic acid groups further contribute to increasing the water solubility of carboxy methyl dextran. Carboxy methyl dextran is more hydrophilic than cellulose.

In our study, concentration pulses of the model colloidal pitch suspensions were injected sequentially into the aqueous stream flowing over the same CMD surface. Short carboxyl methyl dextran chains (100 nm) are covalently grafted over the thin gold film uniformly covering glass.

1) Surface Plasmon Resonance Study

In our surface plasmon resonance study (SPR), four successive pitch pulses of increasing concentration were injected over the same surface so as to reproduce the effect of slow build up on pitch deposition. The sensograms are shown superposed (offset) for clarity. The sensogram indicates the mass of pitch in the surface vicinity (100nm thick interphase) as a function of time. Only a horizontal translation was applied to the sensograms; so the initial value of the baseline of the second sensogram corresponds to the final value of the first injection.

A sensogram is typically made of 3 distinct sections: 1) an absorption phase, 2) a plateau, and 3) a desorption phase. The shape of the initial sensogram adsorption phase results from the balance of material transport and its affinity for the surface as the initial front of the concentration pulse flows over the area monitored. At a given flow rate and concentration, the initial slope is a direct indication of the adsorption constant. In the second phase, a maximum concentration is reached, once the CMD interphase is saturated with pitch, or once the equilibrium surface-liquid is reached. The shape and slope of the onset-plateau are mainly dictated by the balance of the adsorption and desorption constants. The duration of this second phase is established by the amount of material injected and the flow rate. The last section of the sensogram corresponds to the drop in concentration associated with the end of the pulse and represents the material removal or the disassociation phase. This phase best describes the affinity of the substance for the surface. The faster this decay, the weaker is the interaction between the pitch and the surface. At the end of the pulse, the baseline typically decays as the pitch particles are sheared off by the continuous liquid flow, and levels-off; the faster the decay, the weaker the pitch-surface interaction. A substance adsorbed strongly or irreversibly on the surface has a higher final baseline than its initial baseline; the higher the final baseline, the more substance remained on the surface.

The effect of pitch concentration and build-up at 20°C on a CMD surface was investigated by injecting four successive pulses of increasing concentration on the same carboxy methyl dextran surface. The superposed sensograms are shown on Figure 4. Three observations are of interest. The first is that the signal responses for the pitch pulses are all very low. The signal response is typically of 1000 relative units (RU) per ng/mm^2 of material adsorbed (*26,27*). Responses of 500 to 5000 RU are typical but the increase in relative units achieved with pitch was only about 130 RU. The second observation is that the sensograms are independent of the concentration of pitch injected and all very similar, with the exception of

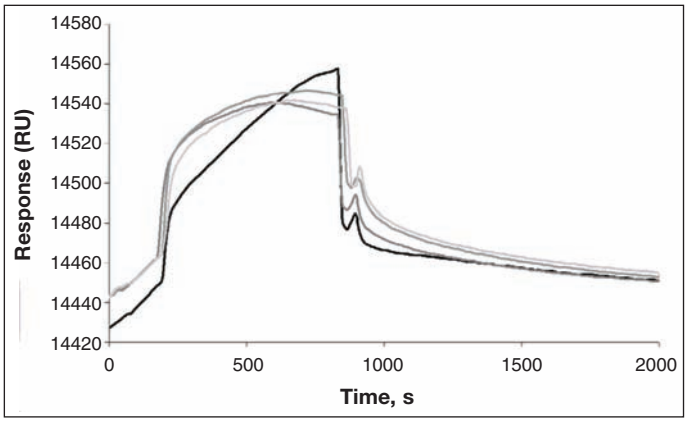

Fig. 4 Superimposed sensograms of four consecutive pitch pulses of increasing concentration (40, 80, 120 and 160 mg/L) on CMD surface at 20°C. The lighter the line, the higher the concentration (black = 40 mg/L, pale grey= 160 mg/L).

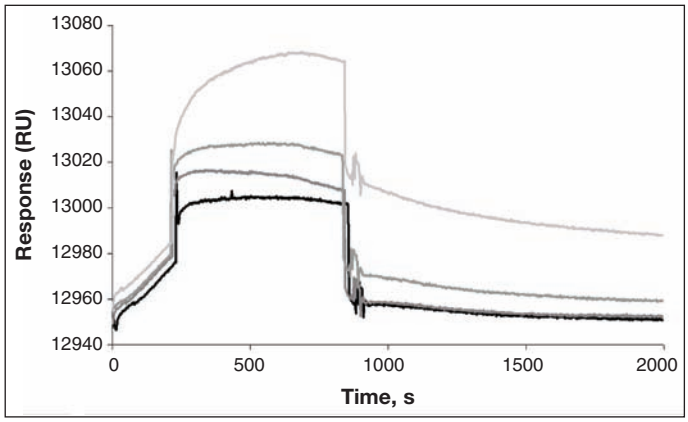

Fig. 5 Superimposed sensograms of four consecutive pitch pulses of increasing concentration (40, 80, 120 and 160 mg/L) on CMD surface at 30°C. The lighter the line, the higher the concentration (black = 40 mg/L, pale grey= 160 mg/L).

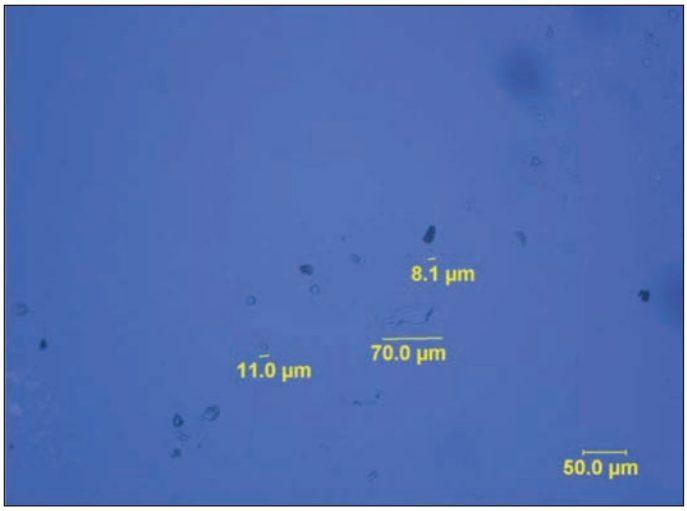

Fig. 6A Micrograph showing large and small pitch particulates magnified (X100).

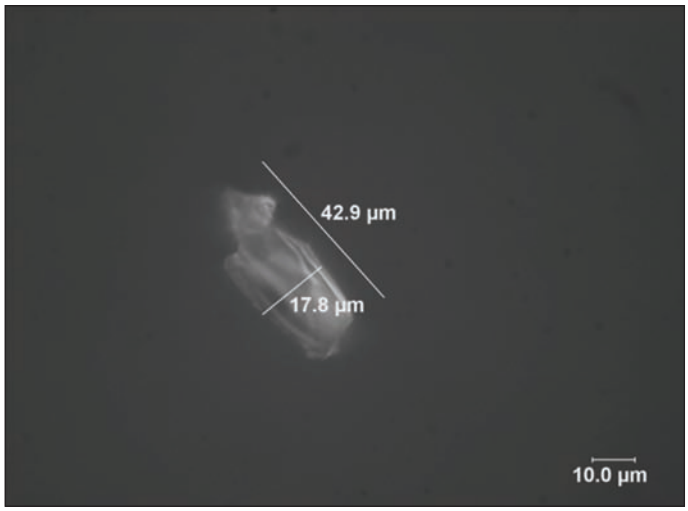

Fig. 6B Micrograph of a large pitch particulate magnified at X100.

the first. The first injection interacts differently and passivates the fresh CMD surface. Thus all subsequent pitch pulses are interacting with a surface previously modified by pitch deposition. The third observation is that colloidal pitch adsorption on CMD is very weak, as indicated by the rapid drop in pitch concentration corresponding to the end of the injection pulse. The micro-fluidic cell provides sufficient shear to remove most pitch deposits.

The effect of temperature on pitch deposition was also studied, by performing the same experiment at 30°C (Fig. 5); a new CM5 chip was used. A few observations are worthwhile. First, the sensograms are all different and concentration dependent. Second, the response signal remains low and similar to that at 20°C. Third, pitch adsorbs at 30°C on CMD surfaces and the amount increases non-linearly with the liquid pitch concentration or with the number of previous pitch pulses injected. This can best be seen with the increase level of the final baseline. The shear created by the eluent flow slowly desorbs the pitch, but never completely; the final baseline never drops to its initial level. The increase in height of the final baseline for each sequential pitch injection suggests that pitch has a low affinity for the CMD surface but a higher affinity for pitch modified surfaces.

2) Pitch suspension characterisation

The pitch suspension was characterised by optical microscopy. A wide distribution of pitch particle size and shape was observed (Fig. 6). Spheres and plates were the most common shapes. The critical dimension of the particles ranged from 1 to 40 μm (Fig. 6A). Larger particles were also observed (Fig. 6B). There is an order of magnitude difference between the size distribution of particles in this study and the 0.1 to 2 μm colloids reported in the literature (Table I). Plate-like particulates like the one in Figure 6B would be expected from the recrystallisation of fatty acids.

Table II
Composition of pitch in standards as measured by GC analysis

Concentration	Components			
	Fatty acids (mg/L)	Resin Acids (mg/L)	Triglycerides (mg/L)	Total (mg/L)
X	10	23	10	43
2X	20	46	20	86
3X	30	69	30	129
4X	40	192	40	172

The chemical composition of the acetone-pitch solution suspensions was analysed by gas chromatography (GC). The pitch acetone solution contained 2.61 mg/mL total fatty acids, 5.83 mg/mL total resin acids and 2.37mg/mL triglycerides; no steryl esters were detected. The calculated composition of the aqueous pitch suspensions are presented in Table II. The pitch particles were made of fatty acid, resin acid and triglycerides in the ratio 1:2:1.

DISCUSSION

For the first time, the adsorption dynamics of colloidal pitch onto a polysaccharide surface was measured in real time at the liquid-solid interface in conditions relevant to papermaking. The model used allows only for the measurement of the effect of chemical interaction, without mechanical entrapment contribution. The hydrophilicity of CMD is expected to be very similar to that of hemicellulose but higher than that of cellulose.

Pitch particles showed very little affinity for the carboxy methyl dextran (CMD) grafted surfaces at neutral pH and 20°C at the solid-water interface. Little permanent adsorption, if any, resulted at equilibrium when the CMD surface was submitted to a pulse of pitch colloids. This follows expectation as there is little driving force for the hydrophobic pitch particles to adsorb onto a hydrophilic CMD surface to decrease their energy. Likewise, wood fibres are not expected to be good adsorbents for pitch. Conditions of high ionic strength, destabilising pitch and low pH (below COOH pK_a of 4.6), preventing the deprotonation of the fibre's carboxylic groups, could allow more pitch adsorption. While thermodynamics do not favour pitch deposition onto fibres at equilibrium, the kinetics process deserves further attention. Upon adsorption, the pitch colloids desorbed steadily when submitted even to a low shear. Pitch adsorption, driven by the high collision frequency with the surface, is a very fast process, while desorption is a slow one. In the timeframe of papermaking this means that many pitch particles adsorbed or entrapped by the fibres might not have the time required to desorb during the time frame of papermaking, while on the wire (1-10 seconds).

While the affinity of colloidal pitch for CMD at 20°C is low, the pitch affinity for the pitch covered surfaces is significantly higher. Any pitch particle adsorbed onto pulp fibres will act as a nucleation centre for other pitch particles to deposit. Since adsorption is fast and desorption is much slower, a substantial amount of pitch could still be weakly adsorbed onto pulp fibres at the end of the forming fabric. However, these pitch clusters, having a high orthogonal projection and a weak adhesion with the pulp surface, will be very prone to desorb once submitted to shear. The desorbed pitch might remain as aggregates instead of colloids. This could lead to significant pitch deposits in the first press nip. It is crucial to keep all surfaces of the paper machine clean at all times to avoid catastrophic pitch build-up.

A previous study with model pitch emulsions has shown that the adsorption of pitch particles is very size dependant (*28*). This suggests that shear plays a critical part in the pitch adsorption and desorption process, which is well known for filler and fines retention. Very little permanent pitch retention resulted- if any- for the large pitch particles onto CMD at 20°C; permanent adsorption was slightly higher at 30°C. However, low levels of pitch were found to remain adsorbed on the CMD surface for the small model pitch colloids (*28*). The question is whether this pitch first adsorbs as colloids or as individual molecules of fatty acid and resin acids. The concentration of free molecules of fatty acid and resin acid dissolved in water must be independent of the pitch colloid size, but dependent upon temperature as thermodynamics dictates the partition equilibrium between dissolved molecules and colloids for the fatty and resin acid forming pitch. Therefore, the different adsorption levels of strongly adsorbed pitch onto CMD, that we observe between the small and the large particles must be due to colloid retention, rather than molecular adsorption, as the concentration of dissolved fatty/resin acid is constant. This suggests that pitch first adsorbs on a surface as colloids and not as individual molecules of fatty and resin acids. This deduction is also supported by the near water insolubility of the pitch components.

The pitch colloids size and shape were affected either by the pitch chemical composition or by the precipitation mechanism. In our study, either the absence of steryl esters, able to prevent perfect packing of molecules, or the fast addition rate of pitch into water could have lead to the crystallisation of the resin and fatty acids into large platelets up to 50μm. Such macro colloids can easily be coagulated by polymers and removed by sedimentation, filtration or by membrane technology. This opens new prospects for enzymatic and microbial wood chip treatments prior to refining. Furthermore, mechanical pulping releases not only pitch but also oligomers of hemicellulose, well-known to adsorb onto pitch colloids (*7,14*). The affinity of hemicellulose stabilized pitch for polysaccharide surfaces is expected to be significantly higher than that of pure pitch; this deserves further investigation.

CONCLUSION

The direct adsorption of pitch particles onto pulp fibres was investigated as a pitch control strategy. For the first time, the adsorption dynamics of colloidal pitch onto a polysaccharide surface was measured in real time at the liquid-solid interface in conditions relevant to papermaking. The adsorption dynamics of colloidal pitch onto carboxyl methyl dextran (CMD) surfaces was analysed by surface plasmon resonance (SPR) spectroscopy and optical microscopy. Surfaces fully grafted with short carboxy methyl dextran chains (around 100 nm) were chosen as a model of the cellulose and hemicellulose fractions of the pulp fibres; this was to dissociate the effect of retention by chemical interaction from the physical entrapment. The effect of pitch concentration, temperature and sequential adsorption cycle was quantified.

The direct adsorption of colloidal pitch onto pulp fibres is not a viable option for pitch control strategy in papermaking. This is because of the very low chemical affinity of pure colloidal pitch for polysaccharide surfaces. Virtually no pitch remained adsorbed at equilibrium over CMD at 20°C; slight retention occurred at 30°C, probably due to mechanical entrapment of the soften pitch. In spite of its low affinity for polysaccharides surfaces, colloidal pitch can be carried by fibres as the low desorption rate might not allow full particle desorption during the time frame of papermaking.

Pitch has a stronger affinity for pitch covered surfaces than for polysaccharides such as carboxy methyl dextran. The proposed mechanism is that pitch first adsorbs as colloids - not as fatty/resin acid molecules- which then serve as nucleation

centres for further colloidal pitch adsorption. It is therefore critical for the papermaker to prevent equipment passivation by keeping all surfaces clean.

Pitch adsorption slightly increased with temperature. This might be caused either by diffusion/reorientation of the molecules changing the surface composition of pitch, or by mechanical entrapment of the softening particles.

The pitch colloids size and shape are functions of chemical composition or the precipitation mechanism. Removing the steryl ester fraction or the fast addition rate of pitch/acetone in water lead to the formation of large platelets which can easily be coagulated and removed by sedimentation, filtration or by membrane technology. This opens new prospects for enzymatic and microbial treatments of the wood chips prior to refining.

ACKNOWLEDGEMENT

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